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Published:  
— without international search report and to be republished upon receipt of that report
- (71) Applicant (*for all designated States except US*): KONINKLIJKE PHILIPS ELECTRONICS N.V. [NL/NL]; Groenewoudseweg 1, NL-5621 BA Eindhoven (NL).  
For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.
- (72) Inventor; and
- (75) Inventor/Applicant (*for US only*): VAN DEN HOOGEN-HOF, Waltherus, W. [NL/NL]; Prof. Holstlaan 6, NL-5656 AA Eindhoven (NL).



WO 02/073156 A2

(54) Title: SAMPLE CONTAINER, MEASURING DEVICE AND METHOD FOR X-RAY ANALYSIS OF LIQUIDS

(57) Abstract: The partial evaporation of the sample liquid during X-ray analysis of liquids gives rise to problems, since the quantity of the sample liquid does not remain constant and evaporated gas is liable to invade the measuring paths in which it may lead to measurement falsifications. In order to solve this problem, there is provided a sample container for receiving a sample liquid, which container leaves open an opening at its top, and a cover is placed on the free surface of the sample liquid. The cover is not rigidly connected to the wall of the sample container and, therefore, allows pressure equalization. Evaporation phenomena are almost completely precluded as a result of the covering of the liquid surface.



## Sample container, measuring device and method for X-ray analysis of liquids

The invention relates to a method for the analysis of liquids by means of X-ray spectrometry, in which method a liquid sample is introduced into a sample container provided with an opening at its top, the sample container is positioned in a sample holder and the liquid sample is analyzed. The invention also relates to a corresponding measuring device  
5 as well as to a sample container in conformity with the introductory part of claim 1 and used to carry out the method.

In practical X-ray analysis use is made of known sample containers in which liquid samples can be introduced so as to be examined via a zone of the container wall which is transparent to X-rays, said zone usually being the very thin bottom of the container. A  
10 problematic aspect of such analyses is that, due to the evaporation of the sample liquid, the quantity of sample does not remain constant during the measurement. Moreover, the evaporated gas components are liable to invade the optical path between the sample and the X-ray source or the detector, thus falsifying the results. Therefore, it would be desirable to use completely closed sample containers. Unfortunately, such sample containers cannot be  
15 used for such measurements, because the measurements usually must be performed under reduced pressure, so that container an excess pressure relative to the surroundings would arise in a closed sample container. This would lead to destruction of the sample container, because the walls thereof must at least locally be constructed so as to be extremely thin for X-ray analysis, so that they break already in the case of very small pressure differences.

20 US 5,351,281 discloses a sample container in which the opening at the top is closed by means of a microporous film which prevents the escape of possibly undesirable substances of the sample from the container, but still allows a gas exchange so that the pressure differences capable of destroying the container cannot occur between the sample and the surroundings. However, containers of this kind do not prevent the evaporation of sample  
25 material and, therefore, are not very well suitable either for the analysis of very volatile liquid samples in particular.

It is an object of the invention to provide a method for the X-ray analysis of liquids, a corresponding measuring device as well as a sample container to be used therein, which method, device and container enable a reduction of the evaporation of sample material

and also the execution of measurements at different pressures out without giving rise to destruction.

This object is achieved in accordance with the invention by means of a sample container as disclosed in the characterizing part of claim 1, a measuring device as disclosed  
5 in the characterizing part of claim 7, and a method as disclosed in the characterizing part of claim 8.

Because of the use of a cover which is arranged on the free surface of the liquid sample in the sample container, no convection from the liquid surface takes place at this area so that evaporation is reduced to a high degree. This holds notably when the cover is  
10 constructed so as to be impervious to gas.

Because the cover preferably covers essentially the entire free surface of the liquid sample, and hence is only slightly smaller than the top opening of the container wall, and is not rigidly connected to the container wall, pressure differences can be equalized without giving rise to excess pressures or reduced pressures in the sample container and  
15 hence to tears. Preferably, use is made of a cover which has a diameter slightly smaller than that of the container opening and is freely movable relative to the container wall. However, a cover which corresponds approximately to the container opening and is attached to the container wall is also feasible when it is flexible and has a small opening for pressure equalization.

In order to ensure that the entire liquid sample is available for the measurement and that the quantity of sample does not change, the cover should not be absorbent, that is, it should not absorb sample material. From a manufacturing point of view it is advantageous to form the cover as a foil which preferably consists of a synthetic material such as polypropylene. However, the cover may also be formed as a sheet, as a cushion or as  
20 a foam.

Evaporation can be precluded practically completely by covering the liquid sample by means of a cover in accordance with the invention. The X-ray analyses then performed are much more accurate and faster. Even when evaporation cannot be precluded for one hundred percent, the evaporation gas remains at least substantially under the cover  
25 and hence does not reach the surroundings, notably the measuring paths.

The development in accordance with the invention, therefore, enables significant improvement of X-ray analysis of liquids. Moreover, the sample containers in accordance with the invention can be manufactured in a rather uncomplicated and hence extremely economical fashion.

## CLAIMS:

1. A sample container for the X-ray analysis of liquids, which container comprises a container wall which forms a cavity for receiving a liquid sample, the container wall being constructed so as to be at least locally transparent to X-rays and leaving open an opening at the top, characterized in that there is provided a cover which is to be arranged on the free surface of the liquid sample and is not rigidly connected to the container wall.  
5
2. A sample container as claimed in claim 1, characterized in that the cover is at least essentially impervious to gas.
- 10 3. A sample container as claimed in claim 1 or 2, characterized in that the cover is not absorbent.
4. A sample container as claimed in one of the claims 1 to 3, characterized in that the cover is a foil.  
15
5. A sample container as claimed in one of the claims 1 to 4, characterized in that the cover consists of a polypropylene material.
6. A sample container as claimed in one of the claims 1 to 5, characterized in that the cover is slightly smaller than the opening at the top of the container wall.  
20
7. A measuring device which includes an X-ray spectrometer for the analysis of a liquid sample accommodated in a sample container, characterized in that it includes a sample container as claimed in one of the claims 1 to 6.  
25
8. A method for the analysis of liquids by means of X-ray spectrometry, in which method a liquid sample is introduced into a sample container comprising a container wall which leaves open an opening at the top, the sample container being positioned in a sample holder and the liquid sample being analyzed, characterized in that prior to the analysis a

cover which is freely movable relative to the container walls is provided on the free surface of the liquid sample.

9. A method as claimed in claim 8, characterized in that use is made of a sample  
5 holder with a cover as claimed in one of the claims 1 to 6.

# PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

# PCT

NOTIFICATION OF TRANSMITTAL OF  
THE INTERNATIONAL SEARCH REPORT  
OR THE DECLARATION

(PCT Rule 44.1)

To:

INTERNATIONAAL OCTROOIBUREAU B.V.  
Attn. Bakker, Hendrik  
Prof. Holstlaan 6  
NL-5656 AA Eindhoven  
NETHERLANDS

02 DEC 2002

COHE

Date of mailing  
(day/month/year)

02/12/2002

Applicant's or agent's file reference

PHNL010126W0

**FOR FURTHER ACTION**

See paragraphs 1 and 4 below

International application No.

PCT/IB 02/00701

International filing date  
(day/month/year)

05/03/2002

Applicant

KONINKLIJKE PHILIPS ELECTRONICS N.V.

1. ☒ The applicant is hereby notified that the International Search Report has been established and is transmitted herewith.

**Filing of amendments and statement under Article 19:**

The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 46):

**When?** The time limit for filing such amendments is normally 2 months from the date of transmittal of the International Search Report; however, for more details, see the notes on the accompanying sheet.

**Where?** Directly to the International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland  
Facsimile No.: (41-22) 740.14.35

For more detailed instructions, see the notes on the accompanying sheet.

2. ☐ The applicant is hereby notified that no International Search Report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

3. ☐ With regard to the protest against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.


4. **Further action(s):** The applicant is reminded of the following:

Shortly after **18 months** from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90b/s.1 and 90b/s.3, respectively, before the completion of the technical preparations for international publication.

Within **19 months** from the priority date, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later).

Within **20 months** from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected in the demand or in a later election within 19 months from the priority date or could not be elected because they are not bound by Chapter II.

Name and mailing address of the International Searching Authority

 European Patent Office, P.B. 5818 Patentlaan 2  
NL-2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Moyra Conner





These Notes are intended to give the basic instructions concerning the filing of amendments under article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the PCT Applicant's Guide, a publication of WIPO.

In these Notes, "Article", "Rule", and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions respectively.

## INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only.

### What parts of the international application may be amended?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

### When?

Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

### Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been/is filed, see below.

### How?

Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Administrative Instructions, Section 205(b)).

The amendments must be made in the language in which the international application is to be published.

### What documents must/may accompany the amendments?

**Letter (Section 205(b)):**

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.



## NOTES TO FORM PCT/ISA/220 (continued)

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped), whether

- (i) the claim is unchanged;
- (ii) the claim is cancelled;
- (iii) the claim is new;
- (iv) the claim replaces one or more claims as filed;
- (v) the claim is the result of the division of a claim as filed.

The following examples illustrate the manner in which amendments must be explained in the accompanying letter:

1. [Where originally there were 48 claims and after amendment of some claims there are 51]:  
"Claims 1 to 29, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers; claims 30, 33 and 36 unchanged; new claims 49 to 51 added."
2. [Where originally there were 15 claims and after amendment of all claims there are 11]:  
"Claims 1 to 15 replaced by amended claims 1 to 11."
3. [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:  
"Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or  
"Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."
4. [Where various kinds of amendments are made]:  
"Claims 1-10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 15, 16 and 17; new claims 20 and 21 added."

### "Statement under article 19(1)" (Rule 46.4)

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

**It must be in the language in which the international application is to be published.**

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)."

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

### Consequence if a demand for international preliminary examination has already been filed

If, at the time of filing any amendments under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the same time of filing the amendments with the International Bureau, also file a copy of such amendments with the International Preliminary Examining Authority (see Rule 62.2(a), first sentence).

### Consequence with regard to translation of the international application for entry into the national phase

The applicant's attention is drawn to the fact that, where upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Offices, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/elected Office, see Volume II of the PCT Applicant's Guide.



## PATENT COOPERATION TREATY

## PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>PHNL010126W0</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT/IB 02/ 00701</b>	International filing date (day/month/year) <b>05/03/2002</b>	(Earliest) Priority Date (day/month/year) <b>13/03/2001</b>
Applicant  <b>KONINKLIJKE PHILIPS ELECTRONICS N.V.</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

## 1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☐ the text is approved as submitted by the applicant.

☒ the text has been established by this Authority to read as follows:

**SAMPLE CONTAINER WITH FLOATING COVER FOR X-RAY ANALYSIS OF LIQUIDS**

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☒ None of the figures.



## INTERNATIONAL SEARCH REPORT

International Application No

PCT/IB 02/00701

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 G01N23/20

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 703 927 A (URBANO ROLAND ET AL) 30 December 1997 (1997-12-30) column 1, line 34 -column 2, line 67 column 5, line 34-45 ----	1-9
A	US 5 630 989 A (SOLAZZI MONTE J) 20 May 1997 (1997-05-20) column 4, line 12-17 column 5, line 12-39 claims 1-3; figures 1,3 -----	1-9
A	US 5 215 701 A (GOULD ARNOLD S ET AL) 1 June 1993 (1993-06-01) column 2, line 50-63; figure 1 -----	1-9



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone.

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*8\* document member of the same patent family

Date of the actual completion of the international search

20 November 2002

Date of mailing of the international search report

02/12/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Huenges, A





# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/IB 02/00701

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 5703927	A	30-12-1997	US	5351281 A	27-09-1994
			AU	6634394 A	08-11-1994
			EP	0801739 A1	22-10-1997
			WO	9424547 A1	27-10-1994
US 5630989	A	20-05-1997	US	5451375 A	19-09-1995
US 5215701	A	01-06-1993	US	5001354 A	19-03-1991



## PATENT COOPERATION TREATY

10 APR 2003

PCT

NOTIFICATION OF THE RECORDING  
OF A CHANGE(PCT Rule 92bis.1 and  
Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

BAKKER, Hendrik  
Internationaal Octrooibureau B.V.  
Prof. Holstlaan 6  
NL-5656 AA Eindhoven  
Netherlands

Date of mailing (day/month/year) 31 March 2003 (31.03.03)	<b>IMPORTANT NOTIFICATION</b>
Applicant's or agent's file reference PHNL010126WO 621216WO	
International application No. PCT/IB02/00701	International filing date (day/month/year) 05 March 2002 (05.03.02)

1. The following indications appeared on record concerning:			
<input checked="" type="checkbox"/> the applicant	<input type="checkbox"/> the inventor	<input type="checkbox"/> the agent	<input type="checkbox"/> the common representative
Name and Address KONINKLIJKE PHILIPS ELECTRONICS N.V. Groenewoudseweg 1 NL-5621 BA Eindhoven Netherlands		State of Nationality NL	State of Residence NL
		Telephone No. +31 40 2743444	
		Facsimile No. +31 40 2743489	
		Teleprinter No.	
2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:			
<input type="checkbox"/> the person	<input checked="" type="checkbox"/> the name	<input checked="" type="checkbox"/> the address	<input type="checkbox"/> the nationality <input type="checkbox"/> the residence
Name and Address PANALYTICAL B.V. Lelyweg 1 NL-7602 EA Almelo Netherlands		State of Nationality NL	State of Residence NL
		Telephone No. +31 40 2743444	
		Facsimile No. +31 40 2743489	
		Teleprinter No.	
3. Further observations, if necessary:			
4. A copy of this notification has been sent to:			
<input checked="" type="checkbox"/> the receiving Office	<input checked="" type="checkbox"/> the designated Offices concerned		
<input type="checkbox"/> the International Searching Authority	<input type="checkbox"/> the elected Offices concerned		
<input type="checkbox"/> the International Preliminary Examining Authority	<input type="checkbox"/> other:		

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer  Silvie STENDER
Facsimile No. (41-22) 740.14.35	Telephone No. (41-22) 338 9926

